Water at a hydrophilic solid surface probed by ab-initio molecular dynamics: inhomogeneous thin layers of dense fluid

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February 18, 2005

Disclaimer

Water at a hydrophilic solid surface probed by *ab-initio* molecular dynamics: inhomogeneous thin layers of dense fluid

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TITLE RUNNING HEAD. *Ab-initio* study of water at a hydrophilic solid surface.

ABSTRACT. We present a microscopic model of the interface between liquid water and a hydrophilic, solid surface, as obtained from ab-initio molecular dynamics simulations. In particular, we focused on the (100) surface of cubic SiC, a leading candidate semiconductor for bio-compatible devices. Our results show that, in the liquid in contact with the clean substrate, molecular dissociation occurs in a manner unexpectedly similar to that observed in the gas phase. After full hydroxylation takes place, the formation of a thin (~ 3 Å) interfacial layer is observed, which has higher density than bulk water and forms stable hydrogen bonds with the substrate. The liquid does not uniformly wet the surface, rather molecules preferably bind along directions parallel to the Si dimer rows. Our calculations also predict

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that one dimensional confinement between two hydrophilic surfaces at about 1.3 nm distance does not affect the structural and electronic properties of the whole water sample.

I. INTRODUCTION

The need for a proper knowledge of solid-liquid interfaces at the atomic scale is present in all areas of science, including crystal growth, lubrication, catalysis, electrochemistry, and materials for sensing applications. In the last years a big effort has been made, both experimentally[1-6] and theoretically[7,8], to gain an insight into the solid/water interface characterization. In both hydrophilic[1-4,7-8] and hydrophobic[4-6] surfaces studies, the existence of an interfacial layer of water with properties different from bulk water has been evidenced. Nevertheless, different experimental approaches lead to different conclusions and the interfacial layer thickness was estimated to be from few Ångstrom[1,4,7] to many molecular layers[5]. In both hydrophilic and hydrophobic surfaces structural deformation of interfacial layer has been reported following a reorganization of the H-bond network: in particular a weakening[9] and an enhancement[3] of this network have been shown for hydrophobic and hydrophilic surface respectively. Moreover, while on hydrophobic surfaces dewetting, resulting in water vapor interfacial region, was observed[5]; close to hydrophilic surface, water has a higher density and its structure and dynamics were compared to that of soopercooled[1-2] water or of amorphous ice[3].

The extremely challenging topic and the difficulty to interpret experimental results, demand for theoretical structural models which may complement and clarify some open questions (see e.g. Ref. 10). The aim of this work is to provide a microscopic structural model of the interface between liquid water and a hydrophilic, solid surface, together with insight into its electronic and bonding properties, using predictive and accurate *ab-initio* simulations. We have chosen to focus on Silicon Carbide[11], for which outstanding progress in fabrication[12] and characterization[13,14] have recently been reported, since it is a promising candidate for biocompatible applications and thus knowledge of the interaction and reactivity of its surfaces with water is essential.

Little is known regarding the reactivity of SiC surfaces with liquid water and it is only very recently that experimental and theoretical studies have been able to characterize SiC surfaces exposed to water

vapor; these investigations have concentrated on the cubic polytype (001) surfaces. Experiments on the Si-rich (3x2)-reconstructed SiC(001) surface[15] showed that dissociation of water molecules leads to perfect passivation of the outermost excess Si layer. These results are consistent with those of *ab-initio* simulations of water molecules on Si-SiC(001)[16,17], which revealed how the dissociation mechanism occurs, i.e. following a monomolecular process at low coverage (1/4 of a monolayer), and involving proton exchange among water molecules at high coverage.

Both experiment[15] and theory[16,17] indicate that the Si-terminated surface of SiC will have a high density of -OH surface groups upon exposure to the vapor phase, thus decreasing reactivity and possibly enhancing the surface hydrophilic character. It remains an open question whether the surface reactivity would be inhibited or altered by the strong hydrogen-bond network of the fluid, in the presence of liquid water. In addition, the structure of the interfacial hydration layer on the hydroxylated Si-terminated surface is not known.

Here we present an atomistic description of the Si-SiC(001) surface/water interface and address several key issues: (i) the difference in reactivity of the clean surface in the presence of vapor or liquid water; (ii) the hydrophilic character of the hydroxylated surface and its impact on interfacial water; (iii) the impact of SiC surface periodicity on water structure and possible changes in SiC electronic and structural properties upon water exposure. We have addressed these questions by carrying out a series of *ab-initio* simulations, which have proven both necessary and accurate in describing water adsorption and dissociation on ionic[18-20] and semiconductor surface[21-24]. Although computationally expensive, a first principles treatment of the inter-atomic interactions in crucial: the complexity of water-surface interactions is very difficult to capture[25] by fitting classical potentials to experimental data, and the possible occurrence of molecular dissociation at the surface cannot be addressed with a classical treatment. In addition, experimental data are often not conclusive and hence there is a great need for predictive microscopic models.

The rest of the paper is organized as follows: in section II we describe the method used to carry out our simulations; results and discussion are presented in section III and section IV contains our conclusions.

II. METHOD

We studied the dynamical evolution of the water/SiC system by using Car-Parrinello (CP) molecular dynamics (MD)[26,27] within the Density Functional Theory (DFT) framework, in the generalized gradient corrected approximation (PBE)[28]. We used non-local pseudopotentials[29], and the electronic wavefunctions (charge density) were expanded in plane waves, with energy cutoff up to 80 (320) Ry. Similar to previous investigations[30], the integration over the Brillouin Zone was performed with the Γ point[31]. We used symmetric slabs (11 atomic layers, 16 atoms per layer, periodically repeated along the (001) direction), with a p(4x4) surface supercell periodicity and the SiC theoretical equilibrium lattice parameters (4.39 Å). In addition to the surfaces, the supercell contained 57 molecules in a volume corresponding to the experimental density of liquid water (~ 1 gm/cm^3). The total number of electrons in the system was 1288.

In our calculations, the Si-SiC surfaces (clean and hydroxylated) and bulk water were first equilibrated separately at room temperature, before being placed in contact. We performed two different sets of simulations: one with flexible water molecules at 300 K[32,33], the other with *rigid* water[34,35] at 350 K[36]. In addition to yielding an improved description of the structural and dynamics of water at 300 K, *ab-initio* MD simulations with rigid water molecules enable the use of time steps about 3 times larger than in a flexible water simulation. We note that the melting temperature of SiC is about 2400 K and that the Si-SiC surface is weakly affected by temperature changes of few tens of K close to room temperature. Therefore the use of 300 or 350 K did not affect the structural and reactive properties of the surface.

We started our investigation by simulating the presence of liquid water on the clean surface, and determined how dissociation and hydroxylation occur; subsequently, in a separate simulation, we studied the wetting of the hydroxylated substrate. We note that simulating surface reactivity with the *liquid* instead of vapor is a rather challenging task, due to the need for equilibrating a sample of water independently, prior to exposure to the surface, and to the much larger number of electrons involved in the calculation. Our simulation was divided into three steps which are pictorially represented in Fig. 1:

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(1) the Si-terminated surface was exposed to a liquid composed of *rigid* water molecules[34] so as to achieve equilibration first, in the absence of reactions; (2) the rigidity constraints were then released to allow for bond-breaking and reactions to occur; (3) liquid water on the fully hydroxylated surface was simulated. In the case of the hydroxylated surface, results obtained with rigid and flexible models did not show any relevant difference. In our simulations, the structural features of the interface, e.g. water rearrangement and dissociation, are observed within the first few ps of our 10 ps simulations. This is an indication that the effects of the surface on water can be detected on a time scale shorter than is usually required for convergence of structural properties of bulk water[32,33].

We finally notice that , in our computational approach, the liquid water is contained between two S-SiC surfaces (periodic replicas) at a distance of about 1.3 nm; thus our calculations allowed to analyze the effect of one dimensional confinement on water structure.

III. RESULTS AND DISCUSSION

In this section we describe what our simulations predict and than present an interpretation of the results.

During the calculation with rigid constraints, we observed an attraction between the water molecules close to the surface Si atoms and the substrate, and the formation of a dative bond between oxygen lone pairs and dangling bonds of the Si dimers. In particular, four water molecules bind to the surface (one out of every two surface dimers) and no longer diffuse; their orientation is overall similar to the one found in the gas phase before dissociation takes place. The *rigid* water approach adopted here, preventing bond breaking, gives an indication of how the reaction proceeds at the surface: first the "pinned" water molecules re-orient and then, as soon as the constraints on the water bond distances are removed, they dissociate.

In our simulations, we observed both the monomolecular and H-bond mediated dissociation mechanisms found for gas phase exposure at low temperature (T < 50 K)[16,17]. Therefore unexpectedly, the surface reactivity of the Si-SiC surface with water is not affected by the hydrogen bond network of the liquid and it is not significantly changed by a temperature increase, up to room temperature. As the

simulation proceeds, proton transfer gives rise to the formation of H_3O^+ ions close to the surface: hydronium ions formed at the beginning of our simulation could release a proton, as expected. However, the formation of some H_3O^+ species also occurred when most of the surface Si atoms had already reacted with water and they appear to be stabilized by the H-bond network of the surrounding fluid. The subsequent, expected release of a proton from the hydronium ion was not detected in this case, as this would have required H_3O^+ to diffuse to clean surface sites, which were unavailable in our sample at this stage of our simulation. Yet, the strong affinity to water shown by the Silicon terminated surface clearly indicates that, for longer simulation times, full hydroxylation of the surface would be obtained. This is consistent with previous experiments[15] and calculations[16,17] showing that complete coverage of the Si-SiC(001) surface with -OH and -H groups is energetically favorable (-3.2 eV/water) in the gas phase.

After determining how hydroxylation occurs, in an independent simulation we investigated the deposition of liquid water on the full hydroxylated surface, and carried out a 10 ps simulation. Some of the possible starting configurations for the hydroxylated surface were discussed in Ref. 17. In this work, we used the geometry with all the -OH groups aligned on one side of the Si dimer rows (see inset in the right panel of Figure 1), i.e. the most stable geometry in the gas phase. The inter-pair –OH distance is about 3.1 Å, as imposed by the underlying SiC lattice parameter; this enables a H-bond interaction between the neighboring –OH groups. Although the hydroxylated surface is expected to be hydrophilic due to the presence of –OH groups, Si-H groups are also present and these are known to be hydrophobic; thus the surface/water interaction will be determined by a complex competition between hydrophobic and hydrophilic effects.

In Fig. 2. we characterize the computed structural and electronic properties of the interface between the hydroxylated surface and water by showing the average oxygen density (2a), the average electronic density (2b) and the number of hydrogen bonds (2c) as a function of distance from the interface. The average oxygen density presents an intense peak at 2.2 Å from the surface oxygens. This enhanced density at the interface has been observed in previous simulations for other hydrophilic[37] surfaces and it is determined by packing forces, and the tendency of water to form a maximal number of hydrogen bonds. The observed interfacial peak is expected to be intense and at a close distance from the surface,

in the case of hydrophilic surfaces, with enhanced wetting of the substrate. Indeed in our study of water vapor on the hydrophobic C-SiC(001) surface[16,17], we found that water molecules weakly interact with the substrate and rearrange their geometry to maximize hydrogen bonding at distances larger than those observed on Si-SiC(001). The increased oxygen density at the H_2O/Si-SiC(001) interface found in our calculations is accompanied by an increased electronic density, as shown in Fig. 2b, which very clearly defines an interface layer of thickness of ~ 3 Å. In this layer, water molecules form a smaller number of hydrogen bonds than in the bulk and at a distance of about 3 Å from the oxygen surface atoms the bulk value of ~ 3.6 H-bond/water is recovered (see, Fig. 2c, where the H-bonds connecting water molecules to the surface hydroxyl groups were not included). As shown by the blue and red curves of Fig. 2c, the water molecules at the surface do not show any preference in accepting or donating H-bonds. This analysis clearly shows that, both from a structural and electronic standpoint, only a thin layer of water (within 3 Å from the surface) is strongly affected by the presence of the surface. Our result is close to that reported in Ref. 1, where a combined experimental and theoretical approach allowed to estimate a thickness of the interfacial water of about 5 Å; the slight difference may be related to the different material and shape (cylindrical glass pores) of the analyzed confining media.

In addition to density changes, another way to measure the extent of water structural changes is by the distribution of the O-O-O angle between neighboring molecules; the computed distribution shows that at a distance of about 3 Å from the surface the preferred coordination is tetrahedral, as in bulk water, whereas at lower distances high and low coordination angles are also favored. This result reinforces the conclusions drawn above, that water molecules recover their equilibrium liquid structure at very short distances from the surface. Only the molecules actually in contact with the surface are strongly affected by the interface and exhibit a coordination number different from the bulk. We note that the water molecules close to the surface do not adopt an tetrahedral structure but rather are arranged so as to optimize their H-bonding network in a manner compatible with the surface -OH orientation and periodicity. This agrees with the experimental analyses drawn in Ref. 38 and do not support the possible occurrence of ice-like ordered structure extending from the solid interface through the confined liquid[3].

In order to gain further insight into the structure of the interfacial surface layer, we have calculated the oxygen spatial distribution function (SDF)[39] in a sphere of 3.0 Å radius, centered either on a –H (red isosurface in Fig. 3) or an -OH group (blue isosurface in Fig. 3); since these groups are close in space the two isosurface slightly overlap in the mid region. The computed SDFs represent the density distribution of oxygen atom positions; thus, in our case, they reveal how water fills the space close to the surface. Fig. 3. shows that water molecules do not wet the surface uniformly, preferring the direction parallel to the dimer row; in other words, the geometry and periodicity of the surface -OH groups induce directionality in the filling space properties of water and ultimately determine the presence of chains of hydrogen bonded molecules bridging over hydrophilic surface groups. The apparent lack of water molecules on top of the -OH group is a steric effect: at a distance smaller than 3 Å, water molecules tend to avoid the axial direction, filling the space around the -OH, where H-bond interactions are more likely to occur. In addition, both the side and top view presented in Fig. 3 illustrates water depletion along the Si-H lines, as expected due to the hydrophobic nature of Si-H.

To assess the effect of the water/surface interaction on the electronic properties of the composite system, we have compared the total electron density of the interface, ρ_{int} , to that of the isolated hydroxylated surface, ρ_{SiC} and of water, ρ_{water}. These densities were calculated for a given snapshot of the MD run in the same simulation cell removing either the surface or the liquid. The changes in electronic charge induced by the water surface interaction can be expressed as: $\rho_{diff} = \rho_{int} - [\rho_{SiC} + \rho_{water}]$. The quantity ρ_{diff} is positive when there is an addition of charge to the system with respect to the isolated fragments, and negative in the opposite case. In Fig. 4a we plot ρ_{diff} for a particular snapshot of the simulation run. The depletion and accumulation of charge, with respect to the isolated water and surface systems, are represented by blue and yellow iso-surfaces, respectively. The main changes in the charge density are localized directly at the interface, and in particular are located along the directions of the hydrogen bonds established between the surface -OH groups and water molecules. The projection of ρ_{diff} on two clip planes containing two different surface -OH groups is shown in Fig. 4b, where we show one group donating (left panel) and the other accepting (right panel) a hydrogen bond. In both cases, we

find a similar trend: upon H-bond formation, the -OH bond polarity is enhanced and the –H atom resides in a positive charge basin (blue spot). At the same time, the electron density in the region of the lone pair of the oxygen accepting the hydrogen bond increases. These results indicate that most of the surface/water interaction is local and strongly related to the capability of the surface to establish H-bonds.

This local character is confirmed by a comparison between the electronic density of states (EDOS) of water, and the hydroxylated surface with that of the interface. This shows that the liquid and solid surfaces are almost decoupled, from an electronic point of view; in particular, the EDOS of the coupled system shows single particle states localized either on water molecules or on the SiC slab. In addition, calculations of the low-lying unoccupied states showed that the energy gap of the hydroxylated surface does not change upon water exposure, thus no difference in the work function should be detected in experiments in aqueous environment, compared to the gas phase.

We finally notice that in our calculations with periodic boundary conditions, liquid water occupies a region about 1.3 nm thick between two solid Si-SiC surfaces. Our results, showing that the effect of a hydrophilic substrate is negligible after 3 Å distance, indicate that one-dimensional confinement effects are negligible or very small on water structural and electronic properties at this scale. It remains to be seen whether confinement in 2 or 3 dimensions would instead bring about notable changes at the nanometer scale. In addition it would be interesting to investigate changes in the dynamical properties of the interfacial water layer, along the lines proposed in Ref. 40, and to investigate whether the changes in viscosity measured[41] for water on soft matter (specifically, on an Au sample coated with a hydrophilically-functionalized SAM) would be observed also in the case of a solid surface/water interface.

IV. CONCLUSIONS

In summary, we have carried out a series of *ab initio* simulations to investigate the interface between liquid water and the clean and hydroxylated Si-SiC(001) surfaces. Surprisingly, we found that at room temperature, the dissociation process of liquid water on the clean surface is very similar to that observed

in the gas phase. The high density of -OH groups present after dissociation lead to a hydrophilic interface and the geometrical arrangement of these groups plays a major role in determining water orientation and eventually the interface wetting properties. A detailed analysis of water structure showed that only molecules within a distance of 3 Å from the hydroxylated surface are affected by the presence of the interface, and that bulk water structure is readily recovered beyond 3 Å. The local nature of the water-SiC interaction is confirmed by electronic structure analyses, indicating that all major changes in the charge density of the isolated liquid and SiC slab are localized at the interface and they pertain to hydrogen bond formation.

The results presented here provide a description of both electronic and structural changes induced in liquid water and SiC surfaces by the presence of the interface, thus yielding a detailed microscopic model of the interface which can be used to understand and devise surface functionalizations for nanoscale devices. This knowledge is still difficult to acquire experimentally, using, e.g. XRD or neutron diffraction data, and most vibrational and spectroscopic measurements of interfacial systems are extremely challenging to interpret in the absence of structural models. By using predictive and accurate *ab-initio* simulations, detailed atomistic models can be obtained, together with insight into the electronic and bonding properties of a solid/liquid interface.
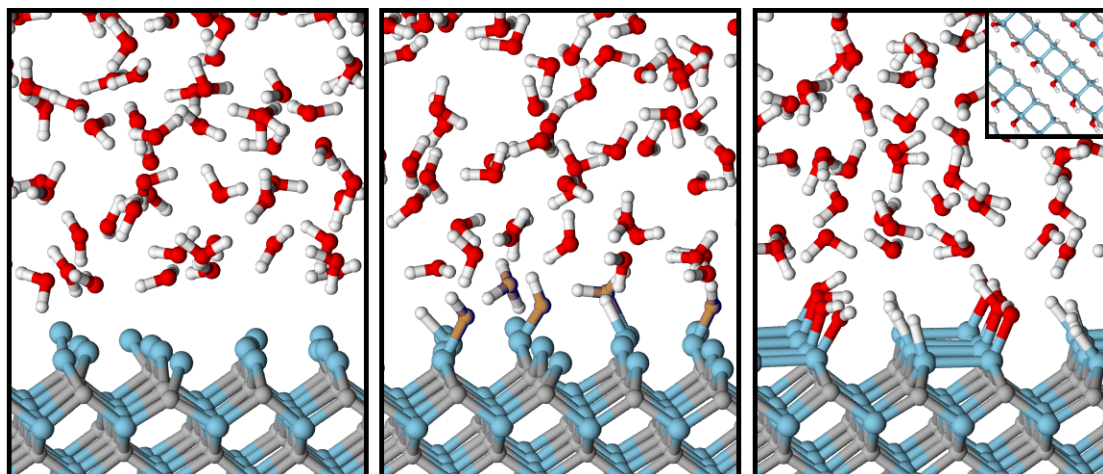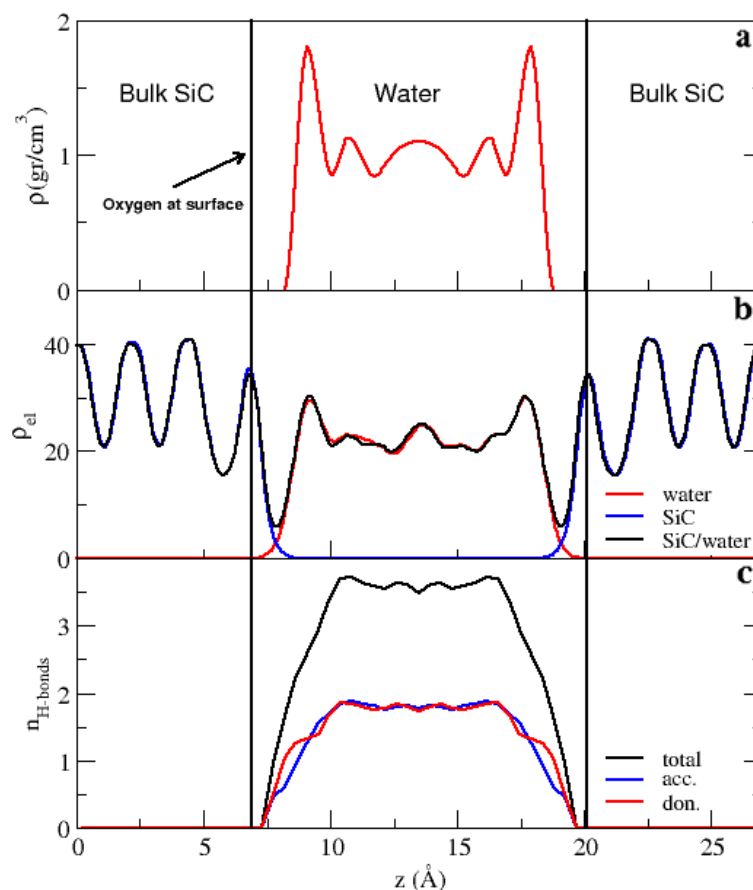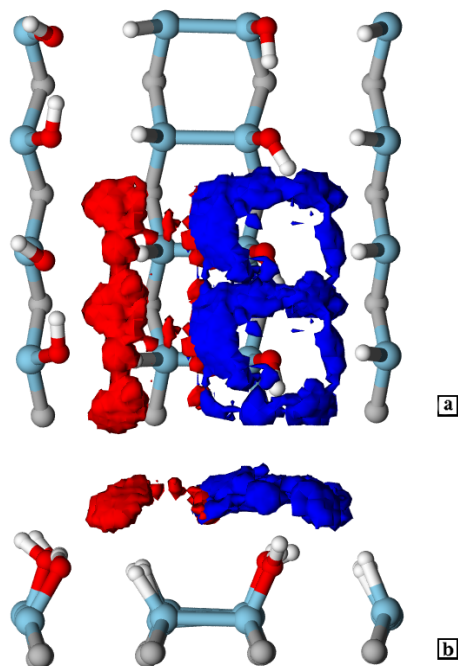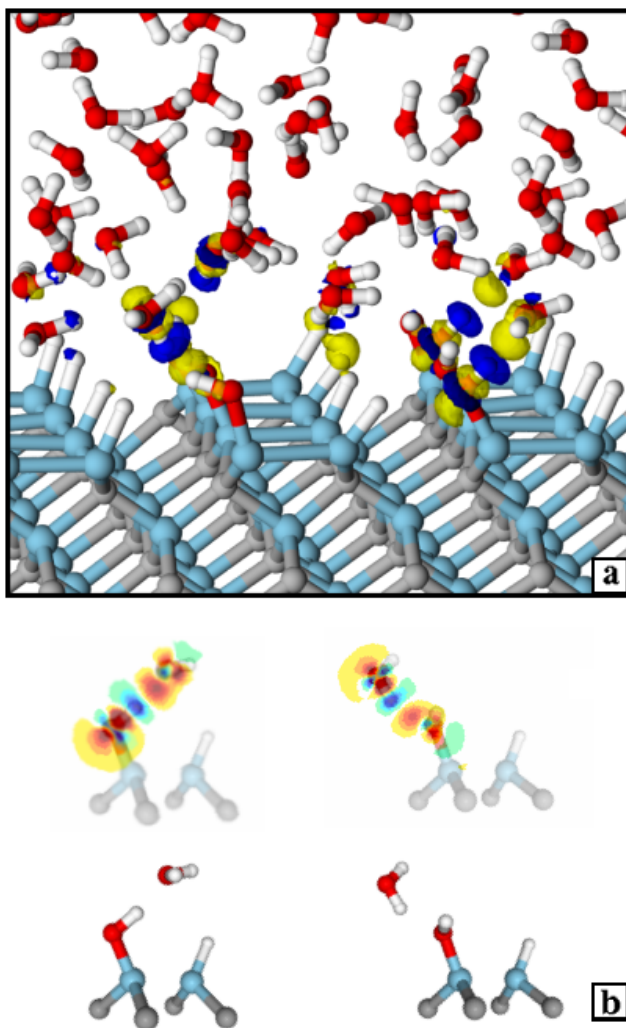
FIGURES

Figure 1. Ball and stick rendering of three representative configurations explored during ab-initio simulations of water deposition on the SiC(001) surface, and of the resulting solid/liquid interface. Red, white, grey and light blue spheres represent oxygen, hydrogen, carbon and silicon atoms, respectively; oxygen atoms in reacting molecules at the interface are highlighted in brown. The left panel shows the clean Si terminated surface [Si-SiC(001)] and the water sample which have been separately equilibrated before being brought into contact. When bringing the solid and the liquid together, in the initial configuration the minimum distance between the Si surface atoms and the water oxygen atoms was chosen to be 2.5 Å: this is the distance at which H_2O molecules start effectively interacting with the surface in the vapor phase, before dissociation occurs. The middle panel shows the reacting water molecules and the formation of hydronium ions at the interface (brown spheres), during dissociation of water molecules. The right panel shows the interface between the hydroxylated surface and liquid water, in the inset a top view of the hydroxylated Si-(SiC) surface is shown..

Figure 2. Average oxygen density (a), average electronic density (b) and average number of water-water hydrogen bonds (c) as a function of the distance from the interface between the hydroxylated Si-SiC(001) surface and liquid water. Water density in panel (a) was normalized to the total number of oxygen. Panel (b) compares the electronic density of the solid liquid interface (black curve) to the one of the water (red curve) and the hydroxylated SiC surface (blue curve); these were averaged in the directions parallel to the interface. The curves in panel (c) were obtained by counting the number of H-bond donor (red curve) or acceptor (blue curve) for each water molecule; the sum of the two curves is also reported (black line). We choose the following geometric criterion to define a hydrogen bond: O···O distance shorter than 3.5 Å and O···HO angle larger than 140º.

Figure 3. Top (a) and side (b) view of the oxygen atom spatial distribution function (SDF) on the -OH (blue isosurface) and on the -H (red isosurface) surface groups; periodic replica are shown for clarity. These SDFs represent the density distribution of oxygen atom positions within two spheres of radius 3 Å centered on the –H and –OH groups. Red, white, grey and light blue spheres represent oxygen, hydrogen, carbon and silicon atoms, respectively.

Figure 4. The upper panel (a) shows iso-surfaces of the electron density difference ρ_{diff} at the interface between the hydroxylated surface and liquid water: $\rho_{diff} = \rho_{int} - [\rho_{SiC} + \rho_{water}]$, where ρ_{int} is the total electron density of the interface as computed within Density Functional Theory, and ρ_{SiC} and ρ_{water} are the electronic charge density of the isolated surface and the fluid, respectively. Yellow (blue) isosurfaces represent charge density increase (decrease) with respect to isolated surfaces. The lower panel shows a projection of the iso-surfaces of the electron density difference onto a clip plane passing through a -OH surface group acting as a H-bond donor (left panel) and acceptor (right panel); the figures shows the stable hydrogen bonds formed between the solid surface and the liquid. Red, white, grey and light blue spheres represent oxygen, hydrogen, carbon and silicon atoms, respectively.

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